REACTION KINETIC MODEL FOR THE TWO-STEP TRANSESTERIFICATION IN THE BIODIESEL PRODUCTION PLANT

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ABSTRACT

Crude palm oil (CPO), which is available in abundant in Malaysia, is used as the feedstock in this research work. The work starts with the analysis of the physical and chemical properties of the feedstock and the associated product to obtain the major fatty acid compositions of triglyceride applicable in the crude palm oil. The kinetic models describing the change in the concentrations of the triglycerides, intermediates, alcohol, and the products during the reaction course are formulated through the corresponding kinetic mechanism. By looking at the kinetic mechanisms of the reaction, the chemical reaction is better understood.

The ultimately proposed kinetic models of the biodiesel production from crude palm oil and methanol under presence of a base catalyst follow the second order differential equations without a shunt reaction. The emphasis of this research work is on the study of the alcoholysis of the crude palm oil under a base catalyst (transesterification) to produce biodiesel at a high quality and a maximum yield. The concentration profiles of the reactants and the products employed in the transesterification are obtained by solving numerically the associated differential equations with introducing the published reaction rate constants applied in a laboratory scale. The effect of the reversible transesterification reaction shows that each concentration profile of the reactants and the products tends to achieve an equilibrium after a certain reaction time.

The simulation results of the kinetics models are implemented in conducting experiments in the pilot plant to produce biodiesel from CPO. Due to impurities such as unwanted gums and pigment, the feedstock must first undergo a physical treatment including degumming and bleaching processes. The high content of water and free fatty acid containing in CPO requires an esterification process. The main objective of this process is to lower that value at a minimum level to avoid the undesired effects such as saponification and inefficiency of the catalyst.

Gas chromatography (GC) analysis method was used to determine the methyl ester contents during the reaction progress. Based on these accurate experiment data along with the simulation results, a validation was done. Technical improvements in the plant operation can therefore be deduced towards the best plant performance and a high quality of biodiesel product.

CONTENTS

1 INTRODUCTION

This chapter deals with the research background and the associated objectives necessary for the research work. The subsequent section sets the scope of works and the intended objectives for completing the tasks. At the end of the chapter, the expected potential applicationis given.

1.1 Research Background

As a plant owner and operator of a biodiesel production plant with a capacity of 1 metric ton per batch, UTHM requires a proper reaction kinetic model for the transesterification of triacylglycerol (TAG) with an alcohol to produce biodiesel with a fuel grade. The advance of a batch mode operating plant is two-fold. The product is of a high quality that meets the fuel specifications and the second one is that the plant can be utilized to examine the potential feedstock and the selection of the best process routes before the commercialization stage. Crude palm oil is selected as the feedstock because it is available in abundant in Batu Pahat. Additionally, Johor is the biggest producer of palm oil within the peninsular of Malaysia. Biodiesel production from crude oil can stabilize the oil prize during the high supply but low deman periodes in the international market. Thus, reasearch activities in the downstream sector of olechemical especially for energy use will bring significantly to the economic contribution in the region. Furthermore, biodiesel is environmental friendly and biodegradable.

Eventhough the importance of biodiesel as an alternative fuel has risen in last two decades, the reaction kinetics of transesterification, the most common process for biodiesel production, is still controversial,Darnoko and Cheryan (2000a);

Freedman et al. (1984). Most efforts in the literatures and journal papers have focused on finding the best fit of empirical data in the lab scale for determination of the reaction order. Unfortunately, some of these results are contradictory. This research attempts to investigate the reaction kinetic mechanisms originated by using the empirical models and an hypothetical model proposed by Komers et al. (2002). Some assumptions must be met due to different system environment such as at a larger scale in which the rate of changes can not be considered as a bulk system, and also the type of feedstock and the catalyst being used.

Gas Chromatography is used for determination and analyse of the fatty acids profile of biodiesel, TAG, monoglycerol, diglycerol, and methanol content. The differential equations initial value problems - describing the transesterfication will then be solved by Runge-Kutta fourth order. The novelty of this research is that starting from the desired specification set by European Norm 14214, the range values of the initial reactant compositions and the residential time can be predicted. Through the two-step transesterification, the conversion of the feedstock to the biodiesel can be better monitored and the desired quality is easier to achieve. Additionally, the energy consumption for the metanol recovery is less due to a minimum excess of methanol in the reaction. The predictive model developed hereby will contribute indeed significantly to the biodiesel plant owner. Furthermore, with the predictive model applied on the actual biodiesel production plant, an optimization problem may be a potential opportunity for the next research area.

Following the stoichiometry, methyl ester or biodiesel is formed through a simple catalyzed reaction of one mole of oil with three moles of methanol. Problems will be encountered if the oil contains impurities and the product purity is of high importance. In the pilot scale where its nature differs from the laboratory one, suitable efforts must be done to prepare the oil free from impurities and useful purification methods must be carried out to obtain the specified product quality.

1.2 Objectives of the Research

The research study embarks on the following objectives:

1. To investigate the real concentration profiles of the triacylglycerol (TAG),

diacylglycerol (DG), monoalcylglcerol (MG), and the methanol result from the experiments in the actual biodiesel plant.

2. To formulate the predictive reaction kinetic equations describing the concentration profiles of the reactants, byproduct and the biodiesel during the transesterification for the biodiesel production in the real plant.

3. To assess the discrepancy of the developed model with the Komers model and transesterification model suggested by Darnoko and Munir Cheryan.

4. To provide the actual equilibrium reaction constants that is necessary how the biodiesel reactor shall be operated to achieve the desired product quality(European Norm 14214) with minimum loss in energy consumption and waste but optimum in yield.

1.3 Scope of the Research Study

To achieve the mentioned research objectives, the scope of the research study is listed as follows:

1. The physical properties data of the feedstock and product are obtained from the published data.

2. The fatty acids composition comprising the palm oil is limited to

   ve major components, myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid. The other minor components are relative to their mass percentage negligible.

3. Transport effects on the rates of concentration change are excluded, since these may complicate, or even obscure, the principal objectives of the work. The concentration gradient within the reactor is therefore spatially negligible.

4. The reaction rate coeficients necessary for solving the partial differential equations numerically are obtained from the experimentally published data.

1.4 Potential Application

The main expected scientific contribution of the research is the application of the two–step transesterification of crude palm oil in the reacting vessels. This method enables the batch–mode operating pilot plant to deliver a high conversion of the feedstock and a high yield of biodiesel under specific process variables. Having the right process variables in the hand, a process engineer can operate the plant more convenient regardless of the various conditions encountered from a batch to another batch, or from a stage to another stage of the transesterification process. Moreover, the underlying knowledge lies in the kinetic models deducted from the reaction mechanism that is better understood.

2 LITERATURE REVIEW

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement fuel oil. Transesterification (esters exchange) is the most common method to solve the problem. It is a chemical reaction of a fat or oil (triglyceride) with an alcohol to form esters and glycerol. This chapter will elaborate the state of the art in the biodiesel production from an initial feedstock to the final product through the literatures reviews.

2.1 Feedstock Properties

Biodiesel can be made from any plant oils with over 350 oil-bearing crops being identified for the production of biodiesel, Ng et al. (2009). The selection of feedstock for biodiesel production depends primarily on region, price and chemical properties. The dominant feedstock varies among countries, since the suitability of vegetation is very much dependent on local climates. The predominant raw material in European countries is rape seed, while in the United States (US) soybean is the most widely used feedstock. For a tropical climate like Malaysia palm oil is the common feedstock for biodiesel production.

Determining the chemical and physical properties of crude palm oil as the feedstock for biodiesel production is of importance for the proper selection of the process routes. Abdul Aziz (2000) as cited in Rohani Mohd Zin (2006) has classified crude palm oil into five physical, chemical groups as shown in Table 2.1. The main component of crude palm oil is triglyceride which composes 90 – 98% of the total mass, Canakci and Sanli (2008). Some of the groups and components

Table 2.1: General Components of Crude Palm Oil

Group	Components
Oil	Triglyceride, Diglyceride, Monoglyceride Phospholipids Free Fatty Acid
Oxidized Products	Peroxide
Non-oil but oil soluble	Carotene, Tocopherol
Impurities	Metal particles
Water solubles	Water (Moisture)
	Glycerol, Chlorophyl pigments

must be removed partially or completely through the refining process to meet the desired feedstock specification. Free fatty acid (FFA) is the fatty acid that is not bound on the glycerol backbone of triglycerides. FFA originates from the breakdown of triglycerides into its component fatty acid and glycerol units, and results from the exposure of triglycerides to moisture or from enzymatic processes. Copeland and Belcher (2002) reveals that a high FFA in a vegetable oil generally indicates that the oil was poorly processed or that there has been some triglyceride breakdown after refining. FFA also indicates the degree of purity of oil. A purer oil posses a lower value of this number. Kima et al. (2002) recommends that phospholipid commonly referred to as gums must be removed because of their strong emulsifying action. This component causes an undesirable flavor and a coloring pigment. The emulsifying action is therefore the main suspect causing the oxidative instability of the crude palm oil. Peroxide is an oxidation product that causes rancidity when the oil reacts with oxygen. The tocopherol and carotene content in oil acts naturally as an antioxidant and makes the oil a reddish brown color. Wei et al. (2004) has investigated that trace metals such as iron (Fe) and copper (Cu) are undesirable and usually resulted from the mechanical wear at the mills and refineries. These metals are pro–oxidant and hence reduce the oil quality. The presence of moisture in oil can hydrolyze the triglycerides into free fatty acids and glycerol leading to an adverse effect in the oil quality as shown in the following reaction:

$$\underset{\text{Triglycerides}}{C_3H_5(OOCR)_3} + \underset{\text{Water}}{3H_2O} \rightarrow \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{FFA}}{3RCOOH}$$

Table 2.2: Typical Compositions of Crude Palm Oil

Composition	Unit	Value
Triglyceride	%	≥ 95
FFA	%	3.5
Diglycerides	%	2 – 6
Colour	-	reddish brown
Moisture and Impurities	%	0.25
Peroxide	meq/kg O_2	1.0
DOBI	-	2 - 3.5
Phosphorus	ppm	15
Iron	ppm	5

Where, R is the long chain fatty acid consisting of the carbon-hydrogen bonds.

Understanding the crude palm oil components as aforementioned is essential in process engineering. The typical compositions of Malaysian crude palm oil is summarized in Table 2.2 as reported in Basiron and May (2005). These compositions certainly will determine the suitability of the crude oil for applications. As shown in Table 2.2, triglycerides are the major component of a palm oil. As evaluated in Basiron (2005), monoglycerides and diglycerides are also present in a small amount as an artifact of the refining process. The fatty acid chains in triglyceride can vary in number of carbons and in structure (single or double bonds). These two factors affect greatly in the chemical and physical characteristics of the palm oil. Knowledge about the detailed structures of the triglycerides present in palm oil is necessary because they define some of the physical characteristics of the oil. The melting points of triglycerides are dependent on the structures and position of the component acids present. They also affect the emulsifying behavior of the oil. The semi solid nature of palm oil at room temperature has been attributed to the presence of the unsaturated fraction.

The partial glycerides are formed in the extraction process. Oil obtained from unbruised sterilized fruits shows trace levels of partial glycerides. Random analyses of samples of refined palm oil, palm olein, and palm stearin have shown the presence of about 6% diglycerides with trace amounts of monoglycerides, (Basiron (2005)). These partial glycerides are important as they are known to affect the crystallization behavior of the oil. Furthermore, the semi solid present in the oil at a normal condition is due to the process of solidification occurring in the oil as a consequence of its chemical properties. The various structures in the molecular triglyceride (saturated and unsaturated) with the associated chemical character-

istics reveal obviously the physical states at that temperatures, hence affecting the melting behavior to the oil. A classical method to measure the degree of the unsaturation in fats and oils is called an iodine value (IV) measurement. Hereby, an iodine-bromide (Hanus reagent) or iodine monochloride (Wijs reagent) reagent is reacted with the double bond and an excess reagent (as iodine) is then titrated with sodium thiosulphate solution to obtain its level of unsaturation.

2.2 Fatty Acids Profiles in Crude Palm Oil

Triglycerides or triacylglycerol making off the major component of the vegetable oils and animal fats are chemically a compound of triesters formed from three molecules of fatty acids with a glycerol molecule as the backbone, as shown in Figure 2.1. Fatty acids consist of the elements carbon (C), hydrogen (H) and oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end.

The functional groups, represented by R_1,R_2,R_3, are fatty acids consisting of the long-chains of carbon-hydrogen bonds. The identity of the three fatty acids in the triacylglycerol determines whether it is oil or fat. Increasing the number of the double bonds in the fatty acid chain decrease the melting point of the triacylglecides. Fats have higher melting points, hence they are solid at room temperature. Oil, in contrast, is liquid at room temperature due to its lower melting points. This different physical phase is affiliated to the double bond of

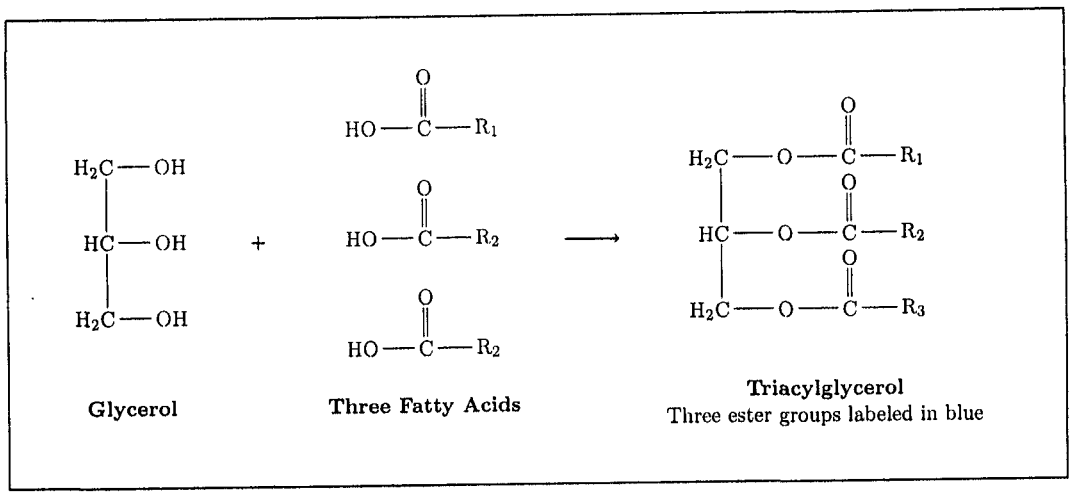
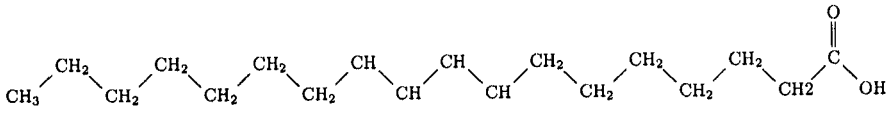
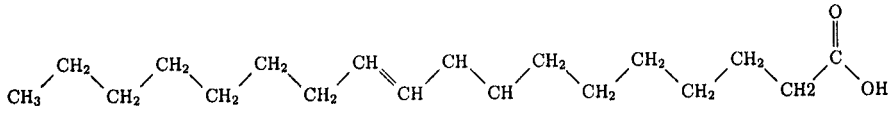


Figure 2.1: Triglycerides from the glycerol backbone with triesters molecules



Stearic Acid ($C_{18}H_{36}O_2$), Melting Point 69 °C, Fat



Oleic Acid ($C_{18}H_{34}O_2$), Melting Point 13 °C, Oil

Figure 2.2: Skeletal structures of stearic acid and oleic acid.

the carbon chain. A large number of double bonds induce a liquid form, whereas fats derived from a few number of double bonds or single carbon-carbon bonds are solid. Fatty acids are called saturated, if they have all the hydrogens that the carbon atoms can hold or do not have any double bond between the carbons.

Figure 2.2 illustrates the difference between two fatty acids in the skeletal structure. Stearic acid consists only a single carbon-carbon bond, called a saturated fatty acid, and oleic acid has one double carbon-carbon bond. It is an unsaturated fatty acid. Hence, oleic acid is oil in room temperature, while stearic acid is fat or solid. Furthermore, fatty acids are frequently represented by a notation such as C18:1 for oleic acid. This notation indicates that the fatty acid consists of an 18-carbon chain and 1 double bond or unsaturated. Stearic acid has a notation C18:0 because it has 18-carbon chain and no double bond or saturated.

The composition of fatty acids in triglycerides may vary depending upon the oil sources. Triolein ($C_{57}H_{104}O_6$) and tristearin ($C_{57}H_{110}O_6$) are examples of simple triglycerides derived from oleic acid and stearic acid, respectively. Man et al. (1999) has observed that triglycerides of palm oil comprise naturally of various fatty acids. It makes the triglycerides being a complex chemical compound. Moreover, fatty acids may combine with any of the three hydroxyl (-OH) groups of the glycerol to create a wide diversity of compounds.

2.3 Biodiesel Properties

Triglyceride means tri–esters of glycerol. Therefore, palm oil contains three ester functional groups ($RCOOR_1$), where R and R_1 represent the alkyl groups. Breaking these tri–esters from the glycerol backbone yields biodiesel. The chemical structure of biodiesel is similar to fossil diesel containing a long chain of carbon and hydrogen. Biodiesel however, contains a few oxygen atoms. As biodiesel made up from various fatty acids components, petrodiesel or diesel fuel comes naturally in a mixture of different petroleum-derived components, consisting of paraffins, isoparaffins, napthenes, olefins and aromatic hydrocarbons, each with their own physical and chemical properties. Petroleum diesel fuels with 9 to 20 carbon atoms have a boiling range between 170 °C and 350 °C, Knothe (2006), whereas biodiesel's boiling points are in the range of 190 °C to 323 °C.

Diesel fuel must satisfy a wide range of engine types, differing operating conditions and duty cycles, as well as variations in fuel system technology, engine temperatures and fuel system pressures. It must also be applicable for a variety of climates. The properties of each grade of diesel fuel must furthermore be balanced to provide satisfactory performance over an extremely wide range of circumstances. In some respects, the substantial quality standards represent certain compromises so that all the performance requirements can be satisfied. By controlling specifications and properties, it is possible to satisfy the requirements of compression ignition engines with a single grade of diesel fuel. The most commonly used guidelines for diesel fuel quality are established by ASTM International in the United States and EN (European Committee for Standard-

Table 2.3: Common fatty acid profiles of palm oil

Fatty acid	**Chemical structure**	**%**	**MP [°C]**	**BP [°C]**
Myristic (14:0)	$CH_3(CH_2)_{12}COOH$	1	54	163.5
Palmitic (16:0)	$CH_3(CH_2)_{14}COOH$	45	62	309.0
Stearic (18:0)	$CH_3(CH_2)_{16}COOH$	4	69	332.6
Oleic (18:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	39	13	334.7
Linoleic (18:2)	$CH_3(CH_2)_4CH{=}CH(CH_2)CH{=}CH(CH_2)_7COOH$	11	-9	230.0

Table 2.4: Fuel Properties of Crude Palm Oil

Properties	Testing Method	Unit	Mean Value
Viscosity at 50 °C	D 445	cSt	25.6
Flash Point	D 93	°C	268
Density at 50°C	D 1298	kg/L	0.889
Gross Heat of Combustion	D 240	kJ/kg	39,690
Sulphur Content	D 4294	wt. %	0.03

ization, CEN) in the European Union. The difference of these two standards are subtle. EN standards are selected for this research purpose because they specify the minimum methyl ester content of biodiesel in the test method. Selected parameters of biodiesel specifications following EN 14214 are listed in Table 2.5 .

Official methods of physical analysis used to characterize conventional diesel are applicable and meaningful when applied to biodiesel and provide useful information. Biodiesel chemistry leads to a number of physical characteristics that are unique when compared with diesel fuels. Most biodiesel preparations have higher viscosity, density, initial boiling point, final boiling point, cold-filter plugging point, and flash point than conventional diesel fuels. Virtually all of these characteristics are due to the high average molecular weight of the component esters of biodiesel. Boiling point and flash point, for example, are related to vapor pressure.

The technical definition of biodiesel is a fuel suitable for use in compression ignition (diesel) engines that is made of fatty acid monoalkyl esters derived from vegetable oils or animal fats. When methanol is used as the alcohol, the biodiesel is produced from these types of oil are called fatty acid methyl esters (FAME). Biodiesel standards are in place in a number of countries in an effort to ensure that only high-quality biodiesel reaches the marketplace. Moser (2009) lists the EN 14214 (European Committee for Standardization, CEN) in the European Union, and summarized in Tables 2.5.

Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats. In general, viscosity is defined as the resistance by one portion of a material moving over another portion of the same material. Dynamic viscosity (η) is defined as the ratio of shear stress existing between layers of moving fluid and the rate of shear between the lay-

Table 2.5: Biodiesel Fuel Standard, EN 14214,Knothe (2006)

Property	Testing Method	Value	Unit
Ester content	EN 14103	96.5 min.	(% w/w)
Kinematic viscosity, 40°C	EN ISO 3104	3.5 – 5.0	mm^2/s
Density, 15°C	EN ISO 3675	860 – 900	kg/m^3
Flash point	EN ISO 3679	120 min.	°C
Sulfur content	EN ISO 20846	10 max.	mg/kg
Cetane number	EN ISO 5165	51 min.	-
Water content	EN ISO 12937	500 max.	mg/kg
Oxidation stability, 110°C	EN I4112	6 min.	h
Acid value	EN 14104	0.50 max.	mg KOH/g
Iodine value	EN 14111	120 max.	g I_2/100 g
Linolenic acid content	EN 14103	12.0 max.	% (w/w)
Polyunsaturated ($\geq$ 4 double bonds)			
Methyl Ester	EN 14103	1 max.	% (w/w)
Methanol content	EN I4110	0.20 max.	%(w/w)
MG content	EN 14105	0.80 max.	%(w/w)
DG content	EN 14105	0.20 max.	%(w/w)
TG content	EN 14105	0.20 max.	%(w/w)
Free glycerol	EN 14105 EN 14106	0.020 max.	%(w/w)
Total glycerol	EN I4105	0.25 max.	%(w/w)
Phosporus content	EN I4107	10.0 max.	mg/kg

ers. The resistance to flow of a liquid under gravity (kinematic viscosity, ν) is the ratio of (η) to the density (ρ) of the fluid. The high kinematic viscosities of vegetable oils and animal fats ultimately lead to operational problems such as engine deposits when used directly as fuels. The kinematic viscosity of biodiesel is approximately an order of magnitude less than typical vegetable oils and is slightly higher than petrodiesel, Gerpen and Knothe (2005); Moser (2009). If fuel viscosity is low, the leakage will correspond to a power loss for the engine. If fuel viscosity is high, the injection pump will be unable to supply sufficient fuel to fill the pumping chamber. Again, the effect will be a loss in power. However, Crabbe et al. (2001) reported that the viscosity of crude oil is about 10 times or higher that of No.2 diesel fuel. This is associated with large triglyceride molecule and its higher molecular mass. After transesterification, biodiesel derived from palm has a viscosity value of 5.0 cSt at 40°C, Demirbas (2006) with the density of 880 kg/m^3 at 15.5°C. Gerhard Knothe (2005) investigated the kinematic viscosi-

ties of the biodiesel fuel components related to the fatty acid parents. Table 2.6 shows the data for the common fatty acids and the corresponding methyl esters measured at 40 °C.

Table 2.6: Viscosity of Fatty Acids and Methyl Esters [mm^2/s]

Fatty acid/Ester	**Fatty Acid Structure**				
	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
Triglycerides	nd	nd	nd	32.94	24.91
Acid	nd	nd	nd	19.91	13.46
Methyl	3.30	4.38	5.85	4.51	3.65

The viscosity of the lower fatty components is not detected (nd) at 40°C due to their high melting point, see Table 2.3. The kinematic viscosity of each methyl ester component is in the range of 3 – 5 mm^2/s that are applicable for diesel engines.

Ester content indicates the completeness of the transesterification. Even after a fully complete transesterification reaction, small amounts of tri-, di-, and monoacylglycerols will remain in the biodiesel product. The glycerol portion of the acylglycerols is summarily referred to as bound glycerol. When the bound glycerol is added to the free glycerol remaining in the product, the sum is known as the total glycerol. Limits for bound and total glycerol are also included in biodiesel standards. EN 14214 requires not more than 0.25% of total glycerol in the final biodiesel product that can be measured using a gas chromatographic (GC) method. Because the glycerol portion of the original oil is usually 10.5%, this level of total glycerol corresponds to 97.1% reaction completion of palm oil.

Cetane number or ignitibility is one of the most important properties of a diesel fuel imparting its readiness to auto ignite at the temperatures and pressures present in the cylinder when the fuel is injected. It represents the ignition quality of a diesel fuel. It measures also an ignition delay of a fuel. Ignition delay is a time period between the start of injection and start of combustion of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed. The cetane number scale clarifies an important aspect of the composition of the molecular structure of the compounds comprising diesel fuel. Long chain, unbranched, saturated hydrocarbons (alkanes)

have high cetane number and good ignition quality while branched hydrocarbons (and other materials such as aromatics) have low cetane number and poor ignition quality. The term *cetane number* is derived form a straight chain alkane with 16 carbons ($C_{16}H_{34}$), or hexadecane, also called cetane, as shown in Figure 2.3.

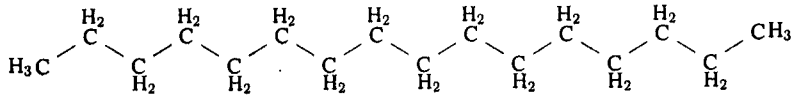


Figure 2.3: Cetane structure, $C_{16}H_{34}$

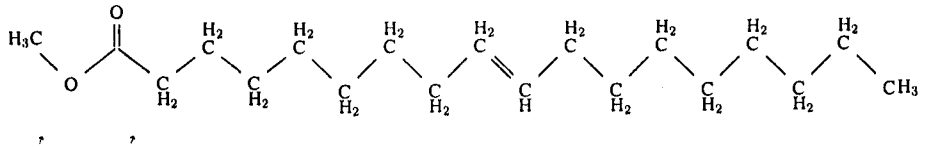


Figure 2.4: Oleic Acid Methyl Ester, $C_{19}H_{36}O_2$

The long unbranched hexadecane is the high quality standard on the cetane scale and has been assigned as having a cetane number of 100. On the other hand, highly branched alkanes are low quality compounds on the cetane scale and have low cetane numbers. Biodiesel's long chain fatty acids methyl ester are similar to long chain alkanes with number of carbons ranging from 14 to 22, for example the oleic acid methyl ester as shown in Figure 2.4. The cetane scale clarifies why triacylglycerols as found in vegetable oils and derivatives thereof are suitable as alternative diesel fuel. The key is the long, unbranched chains of fatty acids, which are similar to those of the n-alkanes of good conventional diesel fuel,Gerpen and Knothe (2005). Demirbas (2006) reported the Cetane Number of palm-based biodiesel at a value of 62 whereas the standard value is 51 minimum.

Water content affects both the oxidative and hydrolityc stability of biodiesel during the storage. Water can be present in a fuel as dissolved water and free water. Petroleum-based diesel fuel can absorb only $\approx$ 50 ppm of dissolved water, whereas biodiesel can absorb as much as 1500 ppm. Although this dissolved water can affect the stability of the fuel, free water is more strongly associated with corrosion concerns. The EN standard limits the amount of water content to 500 ppm. However, biodiesel must be kept dry. Furthermore, water can also contribute to microbial growth in the fuel. This problem can result in acidic fuel and sludge that will plug fuel filters. The higher acid value is caused by the oxidation of biodiesel with air . This change is accompanied by a darkening of the

biodiesel color from yellow to brown and the development of a *paint* smell. In the presence of water, more over the esters can hydrolyze to a long-chain FFA, which also cause the acid value to increase. The reason for auto oxidation is the presence of the double bonds in the chains of many fatty acid compounds. The auto oxidation of unsaturated fatty compounds proceed at different rates depending on the number and position of the double bonds. The species formed during the oxidation process cause the fuel to eventually deteriorate. Excess water in the fuel can lead to not only corrosion but it can also foster the growth of microorganisms.

Flash point for pure biodiesel (120 °C) is much higher than for petroleum diesel (70 °C). Minimum flash points of both biodiesel and petrodiesel are required to meet fire safety specifications. Minimum flash point is set to assure that excess methanol was removed during the manufacturing process, since methanol reduces the flash point. In addition, presence of methanol in biodiesel can also affect fuel pumps, seals and elastomers, and can result in poor combustion properties.

Sulfur content is limited in order to reduce sulfate and sulfuric acid pollutant emissions and to protect exhaust catalyst systems.

Acid number is primarily an indicator of free fatty acids in biodiesel and increases if a fuel is not properly manufactured or has undergone oxidative degradation. Fuel system deposits and reduced life of fuel pumps and filters contribute to an acid number higher than 0.80 that exceeds the maximum value of 0.50.

Free and total glycerin numbers are a measure of the unconverted (triglyceride) or partially converted triglycerides (monoglycerides and diglycerides) as well as by-product triglycerols present in the fuel. High amounts of free and total glycerin can cause fouling in storage tanks, fuel systems, and engines, along with plugging filters and producing other problems.

Phosphorous content in biodiesel, even in a small amount, can damage catalytic converters. Phosphorous levels above 10 ppm are present in some vegetable oils, and this requirement ensures that a phosphorous level reduction process is conducted.

Carbon residue measures the tendency of a fuel to form carbon deposits in an engine.

Thus, biodiesel esters are characterized by their physical and fuel properties

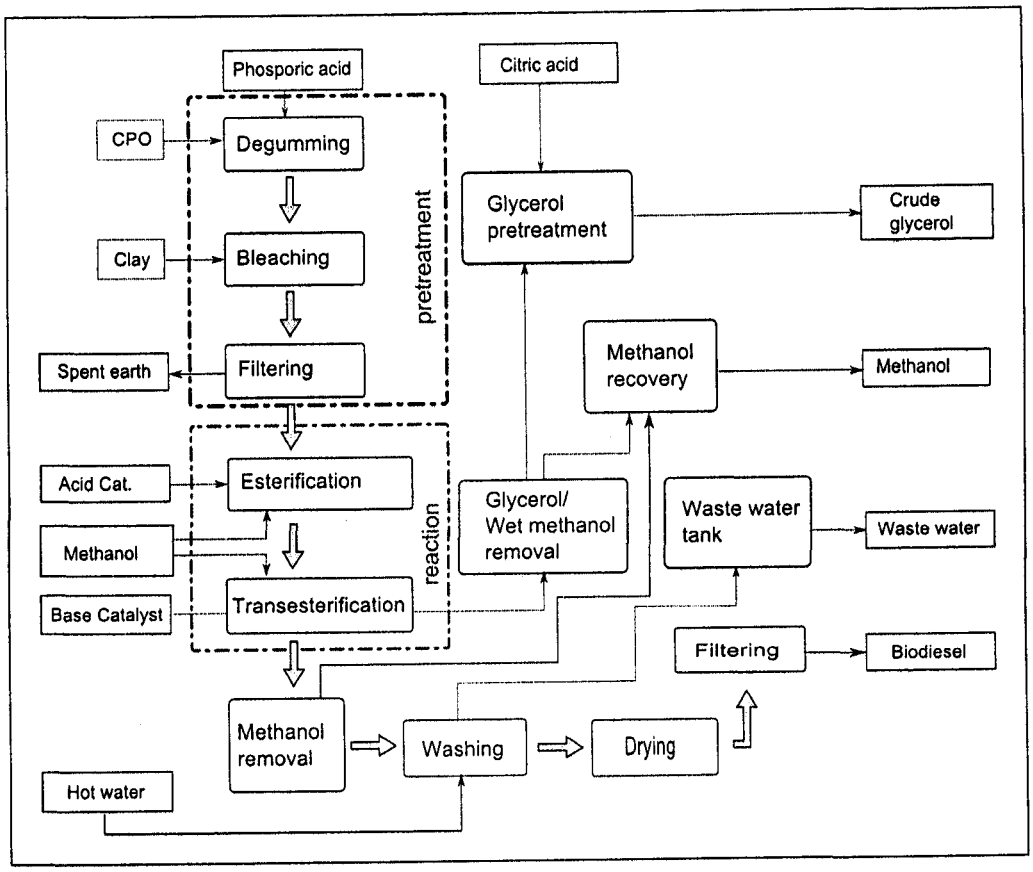


Figure 2.5: Block flow diagram for the biodiesel production

including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque and consume more fuel than No. 2 diesel (D2) fuel. Biodiesel is however better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability, Ng et al. (2009).

2.4 Biodiesel Production

The block flow diagram for the biodiesel production under the study is depicted in 2.5. The production capacity of the plant is 1 MT and operated in the batch mode process. It means that each unit operation operates independently and does not interfere each other. CPO as the feedstock undergoes first the degumming and bleaching processes in the pretreatment section. The intermediate product of this section is known as a bleached palm oil (BPO). The subsequent step is the heart of the plant, the reaction section. It consists of one esterification and

one transesterification reaction. The esterification reactor is operated when the FFA level of the BPO exceeds 1% before transferring it to the transesterification. The reactors operate under an atmospheric pressure and heat supply is provided by a saturated steam generated by a fire tube boiler at a capacity of 500 kg/hr. More over, each unit operation works independently as typical in a batch–mode operating plant.

Purification is the final section to meet biodiesel useful as a fuel. Methanol removal, washing - either water washing or dry washing using an absorbent - and the subsequent drying of the biodiesel before the final filtering are the processes necessary to make the biodiesel quality as per required for a combustion or heating fuel. In the glycerol removal unit operation, the glycerol is neutralized using citrid acid to separate the remaining fatty acid and the crude glycerol. This remaining fatty acid can be esterified to produce biodiesel provided its minimum amount is sufficient. Glycerol itself is a common feedstock for soap production. Furthermore, the waste water produced from the pilot plant is sent to the waste water treatment for a further treatment. Due to hazardous chemicals used in the pilot plant, nitrogen gas must be purged before and after the plant operation for a safety purpose. Methanol, acid and alkaline catalysts are the most flammable liquid that must be prevented from escaping out the process plant.

2.4.1 Pretreatment of Crude Palm Oil

Degumming and bleaching are two essential processes in a palm oil refinery. The purpose is to removal gums, trace metals, pigments, peroxides, oxidation products and other breakdown products in the crude oil as listed in Table 2.1 by adsorption on the active surface of the bleaching earth. The result is in a colour improvement and stability of the final oil as reported in Wei et al. (2004). Hence, bleaching refers to the process in which the colour of the oil is reduced by removal of the colour producing substances including pigments by adsorbent material called bleaching earth.

The main objective of degumming is to remove the unwanted gums, which will interfere the stability of the oil products in later stage. It can be achieved by treating the crude palm oil (CPO) with a specified quantity of food grade acid normally phosphoric or citric acid of certain concentration. The major component of contained in the gums, which has to be removed, is phosphatide. It is vital to remove the phosphatides content in the crude oil because the presence of this

component will impart undesirable flavor and color, and consequently shorten the shelf life of oil. The phosphatides emulsifying action is the main culprit that causes the oxidative instability of the crude palm oil (CPO), Rohani Mohd Zin (2006).

In the degumming unit operation or vessel, the incoming crude palm oil is first heated up to a temperature of about 90 - 110 °C before it is treated with phosphoric acid. The dosage of phosphoric acid normally used is within the range of 0.05 - 0.1 % of oil weight with an acid concentration approximately about 80 - 85 %. The degumming process decomposes the non-hydratable phosphatides as well as to coagulate the phosphatides making them insoluble and thus easily removed during bleaching. Wei et al. (2004) suggested that the crude palm oil is physically mixed with phosphoric acid in an amount of 0.06% by weight ratio. The bleaching earth or clay of a quantity 1% by weight is then introduced into the mixtures to eliminate the gums which transforms the oil into a liquid phase. As result,the bleaching process will endow the colour of the oil in more yellow. The researchers investigated that the percentages of FFA in the degummed and bleached oils for both acid-activated and neutral clays did not show any significant differences from the initial content in CPO. Nevertheless, with the acid-activated clay, the FFA level becomes more or less 0.1% higher than with the neutral clay. Moreover, Edgar Lotero and James G. Goodwin (2004) investigated that spoil proteins containing in CPO are fortunately also removed in the bleaching process.

2.4.2 Reactions

Vegetable oils and animal fats have remarkably similar chemical structures, although they may have different flavor and color. Generally, they are the esters of glycerol in which three hydroxyl groups are esterified by saturated or unsaturated (C_{14} to C_{20}) long chain fatty acids. These trigiycerides can be transesterified to lower the high viscosity of the oil or fat which otherwise may cause the coking of the injectors, oil ring sticking and thickening of lubricating oil. The high viscosity results from the high molar masses of the oils. The transesterification of vegetable oil or fat lowers the molar mas to 30% that of triglyceride. Typically, the cleavage of the oil or fat reduces the molar mass from about 890 to 300 and the viscosity from 20 cSt to 3 – 5 cSt. The reaction can be catalyzed either by a base or an acid. The overall chemistry of transesterification with methanol is represented in Figure (2.7). Overall, it involves the interchange of the alkoxide group between an ester and an alcohol to give a new ester and a new alcohol.

Transesterification can cause unfortunately a soap formation as the negative effect if a base catalyst is employed. To reduce the soap amount, an esterification process is used to lower the free fatty acid content of the oil before performing the transesterification of triglyceride with methanol. Esterification is a chemical reaction for lowering the FFA content to a desired level that is at 0.5% by weight maximum. Water is the byproduct of this reaction. Two types of chemical reaction are therefore necessary in a biodiesel production. The term of methanolysis includes the esterification and the transesterification reactions of triglycerides with methanol as alcohol.

2.4.3 Catalyst

Chemical reaction that proceeds at a normal operating condition very slow, can be accelerated by a foreign material, called catalyst. Catalysts speed up a chemical reaction while itself being unchanged or modified relative slowly, Levenspiel (1999). The activity of many catalysts changes during the reaction progress which it can consequently reduce its effectiveness or become inactive. Vincent et al. (2004) investigated experimentally four different homogeneous catalysts for biodiesel process of sunflower oil with methanol through transesterification reaction. They evaluated the effect of sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), potasium hydroxide (KOH), and potasium methoxide ($KOCH_3$) on the biodiesel purity and yield under a moderate temperature. The results of the study shows that the biodiesel purity under the four catalysts is nearly 100 % after three hours complete reaction. High biodiesel yield is obtained by using the sodium or potassium methoxide at 99.3 and 98.5 wt.%, respectively. However, the product yield decreases under sodium or potassium hydroxide to 86.7 and 91.7 wt.% respectively. This is due to the presence of the hydoxide (^-OH) group that causes a soap formation by the triglyceride saponification. Additionally, Singh et al. (2006) used canola oil as the feedstock in the study of the process optimization of biodiesel production under different alkaline catalysts. They found that the methoxide catalysts gave better yields (94.4 %) compared to the hydroxide counter part (90.2 %). They demonstrated also that all the free fatty acids were converted to soap during the reaction course.

2.4.4 Esterification

M. Berrios (2007), Gerpen and Knothe (2005), and Foon et al. (2004) have investigated that esterification is necessary if the free fatty acid (FFA) level of the oil above 1 % (w/w) which is equivalent to 2 mg KOH per gram of triglyceride. M. Canakci (2001) reduces the recommended acidity to below 0.5%. Gerpen and Knothe (2005) found that the biodiesel yield from unrefined oil will decrease from 93 - 98% to 86 - 87% in the presence of above 5% FFA and ascribed it to phospholipids that destroys the catalyst effect. The esterification of FFA with methanol in the present of an acid catalyst is as shown in Figure 2.6.

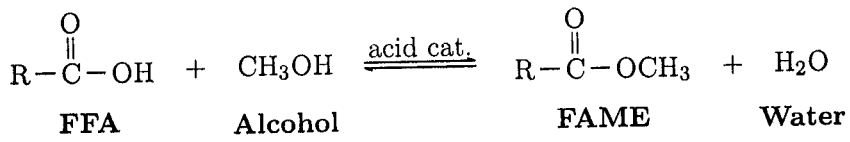


Figure 2.6: Esterification of FFA

Moreover, the FFA and the moisture content are the two major variables dictating the feasibility of transesterifying vegetable oils. Suthat Turapan and Nuithitikul (2010) has investigated the conversion up to 80.7% can be achieved after 8 hours reaction time at 60 °C operating temperature. Palm oil, therefore, is able to be used further for the typical biodiesel production with a base homogeneous catalyst, such as NaOH, to prevent significant formation of soap and yield loss of biodiesel. However, Suthat Turapan and Nuithitikul (2010) recommends to operate at higher temperature than 60 °C for enhancing the reaction rate. Additionally, water generated in the esterification must be removed because it inhibits the forward reaction, thus, it reduces the conversion of FFA to biodiesel. Canakci and Gerpen (2001) showed that an acid-catalyzed pretreatment could be used to reduce the FFA level of the feedstocks to below 1%. Then, these feedstocks could be converted to biodiesel using an alkaline-catalyzed process. A novel feature of this process was that the acid-catalyzed pretreatment was conducted in two or more steps with a separation process between the steps to remove the water formed during the reaction, which inhibits the completion of the reaction.

Crabbe et al. (2001) investigated experimentally the biodiesel production from 25 g of CPO and H_2SO_4 is employed for the catalyst. The researchers obtained for the maximum yield with 97% conversion, the optimized variables shall be at 40:1 methanol/oil (mol/mol) with 5% H_2SO_4 and the the reaction takes place

at 95°C for 9 hours reaction course. Furthermore, Yadav et al. (2010) carried out experiments in 500 mL palm fatty acid (PFA) using 0.2 - 1.2% H_2SO_4 and methanol as the alcohol. The maximum conversion of biodiesel being obtained was 94.4% at a molar ratio 10:1 of CH_3OH to oil and 1% by weight of H_2SO_4 under atmospheric condition and the temperature of a 65°C. The reaction was complete for three hours retention time.

Hayyan et al. (2010) conducted a research study on the effect of catalysts in the esterification of plam oil into biodiesel in a laboratory scale. The researchers found out that para toluenesulfonate, $C_7H_8O_3S$ or abbreviated with PTSA, showed a highest catalytic activity compared to other acid catalyts. 10:1 molar ratio of methanol to oil has been used and FFA content reduced from 25.6% to less than 2% after 90 minutes. The esterification process was used as the pretreatment process before the transesterification using alkaline catalyst. However, 93% conversion of oil to biodiesel has been achieved after two hours reaction time.

Fajriutami et al. (2012) investigated experimentally the esterification of soybean waste cooking oil into biodiesel using ferric sulfate as the acid catalyst. 10 to 16 molar ratios of methanol to triglycerides were used and the mixing speed was at 200 to 400 rpm. They found out that the highest conversion of FFA to biodesel at 90.33 % could be achieved after four hours reaction time under three parameter conditions, namely 16:1 methanol to TG molar ratio, mixing speed at 400 rpm , and 4 wt. % of ferric sulfate.

The esterification reaction of triglyceride with an alcohol is therefore utilized to prepare the feedstock for the subsequent reaction by reducing the free fatty acid level and the water content. The reaction takes place under an acidic condition by introducing an acid catalyst. Moreover, the methanol usage in the reaction is in excess to avoid the reverse reaction.

Kinetics of Esterification of FFA

M. Berrios (2007); Satriana and Dani (2008) investigated the kinetics of esterification of FFA in low grade CPO using sulfuric acid. The researchers concluded that the reaction of esterfication of FFA as formulated in stoichiometric Equation (2.6) is first order in the forward direction and second order in the reverse direction. The change of concentration during the esterification of FFA can accordingly be

formulated as follows:

$$\frac{dC_{\mathrm{FFA}}}{dt} = -k_{1,\mathrm{f}} C_{\mathrm{FFA}} + k_{1,\mathrm{r}} C_{\mathrm{ME}} C_{\mathrm{water}} \tag{2.1}$$

The use of methanol in excess (60:1 molar ratio of methanol to oil) and 5% sulfuric acid concentration relative to FFA, the amount of FFA level can positively be reduced to 1 mg KOH/g oil (0.5 % FFA) within 120 minutes under an operating temperature of 60 °C and 250 rpm or higher. Moreover, the rate constant in the forward reaction ($k_{1,\mathrm{f}} = 50 \times 10^{-4}[\mathrm{mol\ s}]^{-1}$) is 45 higher than that of the reverse counterpart. This fact denotes that the reduction of FFA level takes place faster than the hydrolysis of the methyl ester. Jansri et al. (2011) observed also that the rate constant of the forward reaction in esterification of crude palm oil with a high FFA content (8–12 %) is higher (1.899 L/mol × min.) than that of the reverse reaction (0.684 L/mol × min.).

2.4.5 Transesterification

The majority of the biodiesel today is produced by the alcoholys of triglycerides with methanol by an alkali catalyst, a process frequently referred to as transesterification, Vasudevan and Briggs (2008), Knothe (2006). Suwannakarn (2008) and Gerpen and Knothe (2005) have listed four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits : direct blending with petrodiesel, pyrolysis, micro emulsification, and transesterification. Only the transesterification reaction leads to biodiesel as the product.

Transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, and sunflower seed. Gerpen and Knothe (2005), Freedman et al. (1984) and Gerpen (2005). Darnoko and Cheryan (2000a) and Leevijit et al. (2004) have investigated the transesterification of palm oil to biodiesel in a laboratory scale. Basiron and May (2005) has evaluated the potential usage of palm oil as an alternative feedstock for biodiesel production in Malaysia. According to Darnoko and Cheryan (2000a), there is no published reports on the kinetics of the transesterification reaction of the palm oil in the pilot scale. However, the biodiesel derived from palm oil has been commercialized in Malaysia.

The overall simplified reaction for the transesterification is formulated in a

stoichiometric equation as follows:

$$PO + 3\,M \overset{\text{alk. cat.}}{\rightleftharpoons} G + 3\,E \tag{2.2}$$

Theoretically, to produce methyl ester or biodiesel (E), one mole of bleached palm oil (PO) is required to react with three moles of methanol (M). The reaction takes place under present of an alkali catalyst, and additionally, one mole glycerine (G) is formed as the by-product. Owing of the reversibility of the chemical reaction, the reaction must be devoted to the forward direction. With palm oil is represented by triglyceride, the reaction is rewritten in a structural chemical form yields as follows:

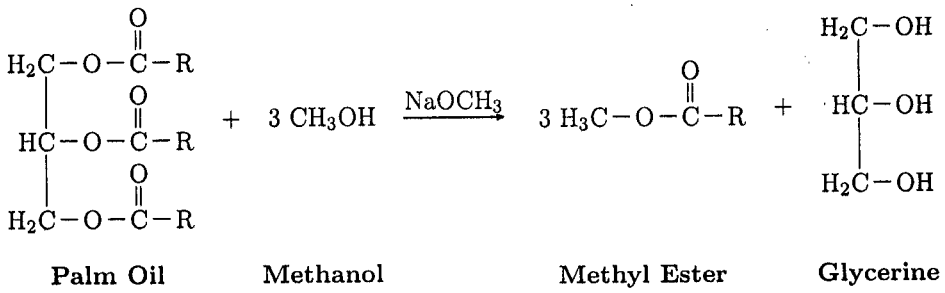


Figure 2.7: Transesterification of a Simplified Palm Oil with Methanol

Figure 2.7 exemplifies the transesterification reaction of an simple palm oil that comprises of the same fatty acids with methanol in a skeletal form. Freedman et al. (1984) investigated experimentally the transesterification of soybean oil in a laboratory scale under present of both the acid and alkali catalysts. In the acid catalyst transesterification with 1% by weight of H_2SO_4, methanol as the alcohol is used in excess (6:1 molar ratio) with five operating temperature conditions, 20°C to 60°C. The methyl ester conversion is below 60% achieved after three hours reaction. However, in the alkali transesterification using 6:1 molar ratio of methanol to oil and 0.5% $NaOCH_3$ catalyst, 93 - 98% conversion has been achieved after 30 minutes reaction. The study examined also that the molar ratio of methanol to oil below 6:1 results in a lower conversion. Transesterification is influenced mainly by catalyst, molar ratio of alcohol to triglycerides, mixing intensity, free fatty acids level, water content and the reaction time. Generally, molar ratios of methanol to triglyceride used have been in the range of 5.25-6:l. Freedman et al. (1984) suggested that, for maximum yield of FAME, a molar ratio of 6: 1 should be used. He also noted that molar ratios greater than 6:1 did not increase the yields of FAME, will make the recovery of FAME and glycerol

complicated, and increase. therefore, the cost of the methanol recovery.

Y. Asakuma and Fukui (2011) studied theoretically the transesterification of triglycerides in terms of the activation energy obtained from molecular orbital calculations. The study included the reactions both under an acid and alkaline catalyst. It was observed that the values of the activation energy under acidic conditions ($\approx$ 25 kcal/mol) were lower than those of basic conditions ($\approx$ 84 kcal/-mol). He explained however the slow reaction under an acid catalyst compared to that under an alkaline catalyst as investigated experimentally in Demirbas (2006); Sharma et al. (2008) due to the formation of a larger, more stable cyclic transition state. Furthermore, he observed that the activation energies for transesterification of diglycerides (78.9 kcal/mol) and monoglycerides (91.2 kcal/mol) are larger than those of triglycerides (93.0). It implies transesterification of MG and DG are harder than TG. This behavior results to an incomplete reaction, and a small portion of diglycrides, and monoglycerides remain in the product Gerpen and Knothe (2005). This fact clarifies the existence of the minor components of mono glyceride and diglyceride at the end of the transesterification reaction.

Additionally, a reaction under an alkali catalyst proceeds at around 4000 times faster than reaction with the same amount of acid catalyst and therefore, it is preferred over the acid catalyst, Sharma and Singh (2008). Therefore, the transesterification reaction can be done in one-step process for oils with FFA within the acceptable range and it should be performed at a minimum of two-step processes for oils with FFA value more than an upper limit. In a two-step process, acid esterification is executed first before the alkali transesterification.

Kinetics of the Palm Oil Methanolysis

Freedman et al. (1986) studied butanolysis and methanolysis of soybean oil. For the methanolysis with 6:1 molar ratio of methanol to oil and usage of 0.5 w/w% of sodium methoxide as catalyst by oil weight and at temperatures between 20 and 60 °C, the experimental data fit better to a combination of a second order consecutive and a fourth order shunt kinetic model. Introducing a shunt reaction into the model implies the simultaneous attack of three molecules of methanol to triglyceride. D. G. B. Boocock and Sidi (1996) and Freedman et al. (1986) discussed and analyzed the difference between the butanolysis and methanolysis of triglyceride. Accordingly. methanolysis takes place only in a two phase reaction, where the oil concentration is very low and the reaction rate is limited by the mass transfer.

Bibliography

A Abdul Aziz. The effect of cpo quality parameters (ffa, m & i, iv, pv, av , dobi and colour) on the refinery production efficiency. In *Proceedings of the 2000 National Seminar on Palm Oil Milling, Refining Technology, Quality and Environment*, pages 79 – 88, Genting Hotel, Genting Highlands, Malaysia, July 2000.

J.E. Andrade, A. Pérez, P.J. Sebastian, and D. Eapen. A review of bio-diesel production processes. *Biomass and Bioenergy, Elsevier*, 35:1008–1020, January 2011.

I. M. Atadashi, M. K. Aroua, and A. Abdul Aziz. Biodiesel separation and purification: A review. *Renewable Energy, ElseVier*, 2011.

Yusof Basiron. *Bailey's Industrial Oil and Fat Products*, volume 6, chapter Palm Oil. John Wiley & Sons Inc., 2005.

Yusof Basiron and Choo Yuen May. Crude palm oil as a source of biofuel: Its impact on price stabilization and environment. Technical article, Malaysian Palm Oil Board (MPOB), 6 Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia, 2005.

Sam Behzadi and Mohammed. M. Farid. Production of biodiesel using a continuous gas-liquid reactor. Technical report, Department of Chemical & Materials Engineering, University of Auckland, Private Bag 92019, Auckland, New Zealand, 2007.

Sumit Bhaduri and Doble Mukesh. *Homogeneous Catalysis: Mechanism and Industrial Applications.* John Wiley & Sons, Inc., 2000. ISBN 0-47-471-37221-8.

Arun Bahl B.S. Bahl. *Advanced Organic Chemistry.* S. Chand & Company Ltd., 1999. ISBN 81-219-0061-1.

M. Canakci and H. Sanli. Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Sociecy for Microbiology*, 35:431–441, 2008.

Mustafa Canakci and Jon Van Gerpen. A pilot plant to produce biodiesel from high free fatty acid feedstocks. In *booktitle*, number 016049. 2001.

D. J. Cole-Hamilton and R. P. Tooze. *Catalyst Separation, Recovery and Recycling.* Number 30 in Catalysis by Metal Complexes. Springer Netherlands, 2006. ISBN 978-1-4020-4087-0. doi: 10.1007/1-4020-4087-3_1.

José A. Colucci, Ernesto E. Borrero, and Fabio Alape. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. 82(7), 2005.

Dick Copeland and W.Maurice Belcher. Methods for recovering fatty acids. *United States Patent*, (US 6,423,851 B1), July 2002.

Edward Crabbe, Cirilo Nolasco-Hipolito, Genta Kobayashi, Kenji Sonomoto, and Ayaaki Ishizaki. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. *Process Chemistry, Elsevier*, 37:65–71, March 2001.

Vinnie Mao D. G. B. Boocock, S. K. Konar and H Sidi. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. 11(11):43–50, 1996. doi: 0961-9534(95)00111-5.

D. Darnoko and Munir Cheryan. Kinetics of palm oil transesterification in a batch reactor. *Journal of American Oil Chem Society*, 77(12):1263–1267, 2000a.

D. Darnoko and Munir Cheryan. Continuous production of palm methyl esters. *Journal of American Oil Chem Society*, 77(12):1269–1272, 2000b.

Boocock David G. B., Vinnie Mao Samir K., Konar, and Hanif Sidi. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. 11 (1):43–50, 1996.

Ayhan Demirbas. Biodiesel production via non-catalytic scf method and biodiesel fuel characteristics. *Energy Conversion and Management, Elsevier*, 65:1–12, 2006.

Ayhan Demirbas. *Biodiesel: a realistic fuel alternative for diesel engines.* Springer-Verlag London Limited, British Library Cataloguing in Publication Data, 2008.